

Mark D'Evelyn



**PCT**

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100 101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200 201 202 203 204 205 206 207 208 209 210 211 212 213 214 215 216 217 218 219 220 221 222 223 224 225 226 227 228 229 230 231 232 233 234 235 236 237 238 239 240 241 242 243 244 245 246 247 248 249 250 251 252 253 254 255 256 257 258 259 260 261 262 263 264 265 266 267 268 269 270 271 272 273 274 275 276 277 278 279 280 281 282 283 284 285 286 287 288 289 290 291 292 293 294 295 296 297 298 299 300 301 302 303 304 305 306 307 308 309 310 311 312 313 314 315 316 317 318 319 320 321 322 323 324 325 326 327 328 329 330 331 332 333 334 335 336 337 338 339 340 341 342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367 368 369 370 371 372 373 374 375 376 377 378 379 380 381 382 383 384 385 386 387 388 389 390 391 392 393 394 395 396 397 398 399 400 401 402 403 404 405 406 407 408 409 410 411 412 413 414 415 416 417 418 419 420 421 422 423 424 425 426 427 428 429 430 431 432 433 434 435 436 437 438 439 440 441 442 443 444 445 446 447 448 449 450 451 452 453 454 455 456 457 458 459 460 461 462 463 464 465 466 467 468 469 470 471 472 473 474 475 476 477 478 479 480 481 482 483 484 485 486 487 488 489 490 491 492 493 494 495 496 497 498 499 500 501 502 503 504 505 506 507 508 509 510 511 512 513 514 515 516 517 518 519 520 521 522 523 524 525 526 527 528 529 530 531 532 533 534 535 536 537 538 539 540 541 542 543 544 545 546 547 548 549 550 551 552 553 554 555 556 557 558 559 560 561 562 563 564 565 566 567 568 569 570 571 572 573 574 575 576 577 578 579 580 581 582 583 584 585 586 587 588 589 590 591 592 593 594 595 596 597 598 599 600 601 602 603 604 605 606 607 608 609 610 611 612 613 614 615 616 617 618 619 620 621 622 623 624 625 626 627 628 629 630 631 632 633 634 635 636 637 638 639 640 641 642 643 644 645 646 647 648 649 650 651 652 653 654 655 656 657 658 659 660 661 662 663 664 665 666 667 668 669 670 671 672 673 674 675 676 677 678 679 680 681 682 683 684 685 686 687 688 689 690 691 692 693 694 695 696 697 698 699 700 701 702 703 704 705 706 707 708 709 710 711 712 713 714 715 716 717 718 719 720 721 722 723 724 725 726 727 728 729 730 731 732 733 734 735 736 737 738 739 740 741 742 743 744 745 746 747 748 749 750 751 752 753 754 755 756 757 758 759 760 761 762 763 764 765 766 767 768 769 770 771 772 773 774 775 776 777 778 779 780 781 782 783 784 785 786 787 788 789 790 791 792 793 794 795 796 797 798 799 800 801 802 803 804 805 806 807 808 809 810 811 812 813 814 815 816 817 818 819 820 821 822 823 824 825 826 827 828 829 830 831 832 833 834 835 836 837 838 839 840 841 842 843 844 845 846 847 848 849 850 851 852 853 854 855 856 857 858 859 860 861 862 863 864 865 866 867 868 869 870 871 872 873 874 875 876 877 878 879 880 881 882 883 884 885 886 887 888 889 890 891 892 893 894 895 896 897 898 899 900 901 902 903 904 905 906 907 908 909 910 911 912 913 914 915 916 917 918 919 920 921 922 923 924 925 926 927 928 929 930 931 932 933 934 935 936 937 938 939 940 941 942 943 944 945 946 947 948 949 950 951 952 953 954 955 956 957 958 959 960 961 962 963 964 965 966 967 968 969 970 971 972 973 974 975 976 977 978 979 980 981 982 983 984 985 986 987 988 989 990 991 992 993 994 995 996 997 998 999 1000 1001 1002 1003 1004 1005 1006 1007 1008 1009 1010 1011 1012 1013 1014 1015 1016 1017 1018 1019 1020 1021 1022 1023 1024 1025 1026 1027 1028 1029 1030 1031 1032 1033 1034 1035 1036 1037 1038 1039 1040 1

**B01J 3/06.**

**(21) International Application Number:** PCT/US00/26704

**(22) International Filing Date:**  
28 September 2000 (28.09.2000)

(74) Agents: SNYDER, Bernard et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).

(25) Filing Language: English

(81) **Designated States (national):** AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, ME, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.

(26) Publication Language: English

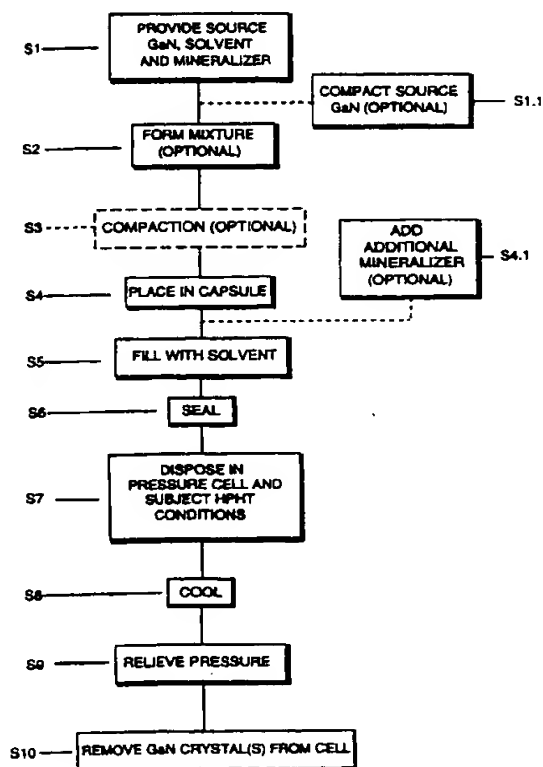
(30) Priority Data:  
09/413.446                      6 October 1999 (06.10.1999)      US

(71) Applicant: GENERAL ELECTRIC COMPANY  
[US/US]; 1 River Road, Schenectady, NY 12345 (US).

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian

[Continued on next page]

(54) Title: CRYSTALLINE GALLIUM NITRIDE AND METHOD FOR FORMING CRYSTALLINE GALLIUM NITRIDE



**(57) Abstract:** A gallium nitride growth process forms crystalline gallium nitride. The process comprises the steps of providing a source gallium nitride (15); providing mineralizer (17); providing solvent (17); providing a capsule (10); disposing the source gallium nitride, mineralizer and solvent in the capsule; sealing the capsule; disposing the capsule in a pressure cell (1); and subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride into at least one gallium nitride crystal. The invention also provides for gallium nitride crystals formed by the processes of the invention.

**WO 01/24921 A1**

patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

**Published:**

— With international search report.

## CRYSTALLINE GALLIUM NITRIDE AND METHOD FOR FORMING CRYSTALLINE GALLIUM NITRIDE

### BACKGROUND OF THE INVENTION

The invention relates to methods for forming crystalline gallium nitride. In particular, the invention relates to methods for high temperature growth of crystalline gallium nitride in a supercritical solvent.

Crystalline gallium nitride is useful as a material for applications in electronic devices including, but not limited to, light-emitting diodes and laser diodes. Currently, gallium nitride (GaN) crystal size and growth, which are produced by known processes, are adequate for some applications, however for many other applications, the gallium nitride crystalline size and quality are not adequate.

Several processes are currently used to produce gallium nitride crystalline substrates. The processes include heteroepitaxial growth of gallium nitride on a substrate, such as a sapphire or silicon carbide. The heteroepitaxial growth process often results in defects, which include, but are not limited to, high concentrations of at least one of dislocations, vacancies, and impurities. These defects may have undesirable and detrimental effects on epitaxially grown gallium nitride, and may adversely influence operation of the resultant gallium nitride-based electronic device. These adverse influences include compromised electronic performance and operation. Presently, heteroepitaxial gallium nitride growth processes require complex and tedious steps to reduce defect concentrations in the gallium nitride.

Known gallium nitride growth processes do not provide large gallium nitride crystals, for example gallium nitride crystals greater than about 0.8 inches (about 2 centimeters) in diameter or greater than about 0.01 inches (about 250 microns) in thickness. Further, the known methods are not known to provide for production of large gallium nitride crystals that result in single-crystal gallium nitride boules, for example gallium nitride crystals of about 1 inch in diameter and about 0.5

inches in thickness, which are suitable for forming wafers. Thus, applications for gallium nitride are limited due to size constraints.

Also, most known gallium nitride crystal production processes do not provide high-quality gallium nitride crystals that possess low concentrations of impurities and dislocations with adequate size and growth rates for electronic device applications. Further, the known gallium nitride crystal production processes are not believed to provide an economical process with nitride growth rates that enable moderate-cost gallium nitride crystal production. Therefore, applications for gallium nitride are further limited due to quality and cost-of-production factors.

Small gallium nitride crystals, such as platelets and needles, have been grown by reaction of nitrogen ( $N_2$ ) gas with gallium (Ga) metal at pressures in a range from about 10 to about 20 kbar and at temperatures in a range of about 1200°C to about 1500°C. The gallium nitride crystalline quality produced by this process may be adequate, in terms of dislocation density, for some gallium nitride applications. The gallium nitride crystalline quality formed by this process, however, exhibits a high concentration of undesirable nitrogen-vacancy defects, which adversely influences certain gallium nitride crystal applications. Additionally, this process appears to be limited to producing a maximum gallium nitride crystal size of about 15 millimeters (mm) to about 20 mm in diameter and only about 0.2 mm in thickness. This gallium nitride production process may also suffer from small gallium nitride crystal growth rates, for example growth rates of about 0.1 mm/hr.

Small gallium nitride crystals, for example in the form of crystalline platelets and/or needles with a size less than about 0.4 millimeters (mm), have been grown in supercritical ammonia ( $NH_3$ ) in pressure vessels. These supercritical ammonia growth processes exhibit slow growth rates, and thus do not enable boules or large gallium nitride crystals to be readily produced. Also, the pressure vessels limit these gallium nitride growth processes. The pressure vessels limit the supercritical ammonia growth process to a pressure less than about 5 kbar, and thus limit the supercritical ammonia growth process temperature and reaction rate.

Gallium nitride growth on an existing substrate has been proposed by a chemical vapor deposition (CVD) process. The CVD process may use reactions, such as, but not limited to,  $\text{GaCl} + \text{NH}_3$  or  $\text{Ga}(\text{CH}_3)_3 + \text{NH}_3$ . These CVD processes are believed to be limited by at least one of: limited capability for growing large, thick  
5 gallium nitride crystals and substrates; poor gallium nitride crystal quality due in part to the use of an existing substrate, such as sapphire and silicon carbide, that may result in an undesirable lattice mismatch; and subsequent low gallium nitride crystal growth rates. These CVD process limits may lead to high costs of gallium nitride growth, which, of course, is undesirable.

10 Further, gallium nitride growth from other processes, such as reacting of gallium and  $\text{NaN}_3$  at elevated pressures, atmospheric-pressure flux growth, and metathesis reactions ( $\text{GaI}_3 + \text{Li}_3\text{N}$ ) have been proposed. These proposed growth processes are believed to be costly, and are not believed to produce high-quality, defect free gallium nitride in crystalline form.

15 Therefore, a gallium nitride crystal growth process that produces gallium nitride crystals of high quality is needed. Further, a gallium nitride crystal growth process that can produce large gallium nitride crystals is needed.

#### SUMMARY OF THE INVENTION

A gallium nitride growth process forms crystalline gallium nitride. The  
20 process comprises the steps of providing a source gallium nitride; providing mineralizer; providing solvent; providing a capsule; disposing the source gallium nitride, mineralizer and solvent in the capsule; sealing the capsule; disposing the capsule in a pressure cell; and subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source  
25 gallium nitride and re-precipitate it into at least one gallium nitride crystal.

Another gallium nitride growth process for forming crystalline gallium comprises providing of providing a source gallium nitride; providing mineralizer; providing solvent; providing a capsule; disposing the source gallium nitride.

mineralizer and solvent in the capsule; sealing the capsule; disposing the capsule in a pressure cell; and subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate it into at least one gallium nitride crystal; cooling the high  
5 pressure and high temperature (HPHT) system; relieving the pressure in the high pressure and high temperature (HPHT); removing the gallium nitride crystals from the high pressure and high temperature (HPHT) system; and washing the gallium nitride crystals in at least one of water and mineral acids.

A further gallium nitride growth process for forming crystalline  
10 gallium nitride comprises providing a capsule that comprises two opposed end units; disposing a seed gallium nitride crystal in one end unit of the capsule; disposing source gallium nitride with mineralizer and solvent in the other end unit of a capsule; disposing solvent in each of the capsule end units; sealing the capsule; disposing the capsule in a pressure cell; and subjecting the pressure cell to high pressure and high  
15 temperature (HPHT) conditions in a high pressure and high temperature (HPHT) system for a length of time sufficient to dissolve the source gallium nitride and re-precipitate it into at least one gallium nitride crystal.

A still further gallium nitride growth process for forming crystalline gallium nitride comprises providing solid or liquefied gallium as the source gallium  
20 material; providing a capsule that comprises two opposed end units; disposing a seed gallium nitride crystal in one end unit of the capsule; disposing the source gallium with mineralizer and solvent in the other end unit of the capsule; disposing solvent in each of the capsule end units; sealing the capsule; disposing the capsule in a pressure cell; subjecting the pressure cell to high pressure and high temperature (HPHT)  
25 conditions for a length of time sufficient to react the source gallium with the nitrogen-containing solvent under the HPHT growth conditions to form gallium nitride; and subjecting the capsule to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the formed gallium nitride and re-precipitate it into at least one gallium nitride crystal.

The invention also provides for gallium nitride crystals formed by each of above the above-described processes.

These and other aspects, advantages and salient features of the invention will become apparent from the following detailed description, which, when  
5 taken in conjunction with the annexed drawings, where like parts are designated by like reference characters throughout the drawings, disclose embodiments of the invention.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flowchart illustrating a gallium nitride growth process, as  
10 embodied by the invention;

Figure 2 is a flowchart illustrating another gallium nitride growth process, as embodied by the invention;

Figure 3 is a flowchart illustrating another gallium nitride growth process, as embodied by the invention;

Figure 4 is a flowchart illustrating another gallium nitride growth  
15 process, as embodied by the invention;

Figure 5 is a part-sectional schematic illustration of a high pressure high temperature pressure cell for gallium nitride growth processes, as embodied by the invention;

Figure 6 is a scanning electron micrograph of untreated, source gallium  
20 nitride powder; and

Figure 7 is a scanning electron micrograph of treated gallium nitride having hexagonal features, which are characteristic of a hexagonal (wurtzite) crystalline lattice structure, which has been grown under a gallium nitride growth  
25 process, as embodied by the invention.

## DESCRIPTION OF THE INVENTION

Crystallized gallium nitride (GaN) grown by gallium nitride growth processes includes the steps of crystallization (precipitation) of source or starter gallium nitride (hereinafter "source" gallium nitride) into crystalline gallium nitride.

5 The gallium nitride growth process, as embodied by the invention, is conducted at high (elevated) pressure and high (elevated) temperature (as described below) in a supercritical fluid solvent, such as a nitrogen-containing solvent, for example at least one of ammonia, hydrazine, or an organic solvent, such as but not limited to, methylamine or ethylenediamine. The term supercritical fluid means a dense gas that

10 is maintained above its critical temperature, which is a temperature above which the gas cannot be liquefied by pressure. Supercritical fluids are generally less viscous and diffuse more readily than liquids, however possess a similar solvative ability of liquids. A nitrogen-containing organic solvent that is a solid at room temperature, such as melamine, may also provide a suitable supercritical solvent under reaction

15 constitutions. The terms poorly crystallized gallium nitride and well-crystallized gallium nitride define degree of crystallinity in the source gallium nitride. For example, poorly crystallized gallium nitride lacks recognizable facets and is characterized by broad x-ray diffraction peaks and an absence of detectable higher order diffraction peaks with d-spacings in a range from about 1.0 Angstroms to about

20 1.6 Angstroms.

The gallium nitride growth process, as embodied by the invention, produces a high-quality gallium nitride, which is essentially defect-free gallium nitride so the gallium nitride defects do not adversely influence its use in various applications. The gallium nitride growth process, as embodied by the invention, will

25 now be discussed with reference to Figs. 1-4 that are flowcharts of gallium nitride growth processes and steps, within the scope of the invention. The illustrated gallium nitride growth processes and steps are merely exemplary and are not intended to limit the invention.

A gallium nitride growth process, as illustrated in Fig. 1, comprises



providing a source gallium nitride, solvent, and mineralizer, in step S1. The source gallium nitride may comprise at least one of poorly-crystallized gallium nitride, well-crystallized gallium nitride, amorphous gallium nitride, polycrystalline gallium nitride, and combinations thereof. The source gallium nitride may be provided "as-is" in its raw form. Alternatively, the source gallium nitride can be compacted into a "pill" in step S1.1.

The source gallium nitride may then be combined with at least one of the mineralizer and solvent to form a mixture in step S2. Step S2 is optional, and the gallium nitride, solvent, and mineralizer can be provided individually to the capsule as separate and distinct un-combined materials in step S4. The mixture, which can comprise gallium nitride and at least one of the solvent and mineralizer, can be optionally compacted into a pill in step S3, however the compacting of the mixture in step S3 need not be conducted in the gallium nitride growth process, as embodied by the invention.

The source gallium nitride, solvent, and mineralizer, whether as a mixture that is compacted or not compacted, are then placed inside a capsule in step S4. Optionally, additional mineralizer can be added to the capsule in step S4.1. The capsule, which will be described hereinafter, can then be filled with a nitrogen-containing solvent, for example at least one of ammonia or hydrazine, or an organic solvent, including, but not limited to, methylamine, melamine, or ethylenediamine, in step S5. The capsule is then sealed in step S6, disposed in a pressure cell, and subjected to high pressure and high temperature (HPHT) conditions in an appropriate HPHT system, in step S7. The HPHT conditions are maintained for a length of time sufficient to dissolve the source gallium nitride and re-precipitate it onto at least one gallium nitride crystal, gallium nitride boule, or gallium nitride crystal seed. Maintaining HPHT conditions yields large single gallium nitride crystals, for example single gallium nitride crystals having a diameter and thickness in a range from about 0.02 inch (about 0.05cm) to about 12 inches (about 30 cm), for example a size in a range from about 2 inches to about 6 inches. The pressure during step S7, as embodied by the invention, is in a range from greater than about 5 kbar to about 80

kbar, and the temperature for step S7 of the gallium nitride crystal growth process is in a range between about 550°C to about 3000°C.

5 The HPHT system is then allowed to cool in step S8 and the high pressure is relieved in step S9. The gallium nitride crystals are removed from the HPHT system and pressure cell in step S10, for example by being washed in water and mineral acids. The mineral acids for washing the gallium nitride crystals include, but are not limited to, hydrochloric acid (HCl) and nitric acid (HNO<sub>3</sub>).

10 The mineralizers, as embodied by the invention, comprise at least one of alkali and alkaline-earth nitrides, such as at least one of Li<sub>3</sub>N, Mg<sub>3</sub>N<sub>2</sub>, and Ca<sub>3</sub>N<sub>2</sub>; amides, such as, but not limited to, LiNH<sub>2</sub>, NaNH<sub>2</sub>, and KNH<sub>2</sub>; urea and related compounds; ammonium salts, such as, but not limited to, NH<sub>4</sub>F and NH<sub>4</sub>Cl; halide, sulfide, and nitrate salts, such as, but not limited to, NaCl, Li<sub>2</sub>S, and KNO<sub>3</sub>; lithium (Li) salts; and combinations thereof. The mineralizers may be provided as solids or as additives dissolved in fluids, such as solvents.

15 The filling and sealing steps, steps S5 and S6 respectively, will now be described. The capsule is filled with a nitrogen-containing solvent, for example at least one of ammonia or hydrazine or an organic solvent, including, but not limited to, methylamine, melamine, or ethylenediamine, without admitting air or water, which are undesirable in the gallium nitride formation process. To fill the capsule in step S5,  
20 without admitting air or water, the capsule is filled and connected to a negative pressure source, such as a vacuum manifold, and evacuated. The capsule is then chilled to a temperature below room temperature (about 72 °F) and vapor-phase solvent can be admitted to the manifold. The vapor-phase solvent then condenses in the capsule. For example, if the nitrogen-containing solvent comprises ammonia, the  
25 condensation can be performed at dry ice or liquid-nitrogen temperatures.

The capsule can then be isolated so as to seal the capsule in step S6 by closing a valve to the negative pressure source. The capsule can then be separated from at least one of the manifold or the valve by a pinching-off step using a cold-welding apparatus, which is well known in the art. The pinching-off step is

particularly effective if the capsule is copper. The integrity of the seal may be enhanced by optional arc-welding.

The capsule and pressure cell comprise any appropriate form that permit the gallium nitride growth process to withstand the high pressures and high temperatures, as embodied by the invention. The HPHT system that applies the high pressures and high temperatures can comprise a press device, which can include at least one of a die and punch. For example, and in no way limiting of the invention, the press device comprises one of a piston-cylinder press; a belt press; a tetrahedral-, cubic-, or octahedral-anvil press; a recessed-anvil press; and a toriod-type press, each of which are known to those of skill in the art.

A further gallium nitride crystal growth process, as embodied by the invention, will be discussed with respect to Fig. 2. A capsule is provided in step S21. The capsule comprises two opposed end units that are separated by a baffle with one or more apertures. A gallium nitride crystal seed is provided in step S22, and disposed in one end unit of the capsule in step S23. Source gallium nitride is provided together with mineralizer and solvent in step S24, and is disposed in the other end unit of a capsule in step S25. Solvent, as embodied by the invention, is disposed in each of the capsule end units in step S26. The gallium nitride growth process then continues with step S6, as illustrated in Fig. 1.

The gallium nitride seed may comprise a gallium nitride crystal. Alternatively, the gallium nitride seed may comprise a gallium nitride crystal that includes a thin film of a suitable protective material, such as platinum, on the gallium nitride seed. The thin protective film prevents dissolution of the gallium nitride seed prior to gallium nitride crystal growth under the elevated pressure and elevated temperatures, as embodied by the invention. The gallium nitride, which is used in the gallium nitride growth process of Fig. 1, may also comprise gallium nitride crystals as the starting gallium nitride in step S1.

Another gallium nitride growth process, as embodied by the invention, comprises spontaneous gallium nitride crystal nucleation from source gallium nitride.

such as gallium nitride powder. This spontaneous gallium nitride crystal nucleation process produces gallium nitride nuclei upon which further gallium nitride crystal growth will occur. The source gallium nitride powder is provided at a "hot end unit" of the pressure cell, which is the end unit of the pressure cell that is disposed to the heat source in the HPHT system. At elevated-pressures and elevated-temperatures, as embodied by the invention, the temperature differential between the cold and hot end units of the pressure cell is in a range from about 5°C to about 300°C. Thus, the source gallium nitride powder is dissolved and recrystallized under the HPHT conditions thus forming spontaneous gallium nitride crystals.

The gallium nitride growth process, as embodied by the invention, may also use solid or liquefied gallium, as a source material, in a hot end of the pressure cell. The source gallium reacts with the nitrogen-containing solvent under the HPHT growth conditions, as embodied by the invention, to form gallium nitride. This alternative gallium nitride growth process, as embodied by the invention, will be described with reference to Fig. 3. In Fig. 3, step S31 comprises of providing gallium at a hot unit of a pressure cell. Next, in step S32, the gallium reacts with ammonia ( $\text{NH}_3$ ) to form gallium nitride ( $\text{GaN}$ ). The process, as embodied by Fig. 3, then proceeds to the HPHT conditions as in step S7.

Another alternate gallium nitride growth process, as embodied by the invention, comprises creating a temperature differential within the pressure cell, in which this process uses a two-zone capsule. The temperature differential may be created by providing a greater degree of heat to one end unit of the capsule compared to the other end unit of the capsule in step S7. This alternate gallium nitride growth process is depicted in the flowchart of Fig. 4. The steps illustrated in Fig. 4 are similar to those in Fig. 1, and the differences between these processes will be explained hereinafter. In the growth process of Fig. 4, the heat source is differentially applied with respect to the pressure cell, as in step S7.1 during the application of the HPHT conditions. This application changes the temperatures applied to the pressure cell and creates differential temperatures therein. End units of the pressure cell can be held at one temperature, for example ambient temperature, while a central portion of

the pressure cell, is heated to an appropriate HPHT temperature. Operation of the gallium nitride growth process conducted with different heat zones, for example those that would define temperature differentials within the pressure cell, provide for varying gallium nitride growth rates.

5                   The differential heating during the HPHT conditions, as embodied by the invention, include, but are not limited to, steps of: asymmetric placement of gallium nitride source in the pressure cell within a lower temperature end of the pressure cell; using an auxiliary heater to heat the source gallium nitride in the higher temperature end unit of the pressure cell; and using a heating source that generates  
10 differential heat at the gallium nitride source end unit of the pressure cell. Another differential heating during the HPHT conditions step comprises providing the gallium nitride source end unit of the pressure cell with a thinner heater element, so this portion of the pressure cell heats up its contents more readily to create the temperature differential.

15                   An exemplary pressure cell 1, as embodied by the invention, is illustrated in Fig. 5. The capsule 10 is illustrated disposed in a HPHT system 100. The capsule 10 comprises two mating end units, 11 and 12, respectively. Sealing gasket materials (not illustrated for ease of illustration) are disposed at one or more end units to prevent leakage from the capsule 10 under HPHT conditions in the HPHT  
20 system 100. In Fig. 5, a source gallium nitride 15 is disposed in the end unit 12. The end unit 12 is disposed proximate a heat source 16, schematically illustrated in Fig. 5.

                  The heat source 16 may include a graphite tube. The heat source 16 is placed in the pressure cell 1 so as to be in thermal communication with the capsule's contents, and pressure medium 119 may be disposed therebetween. The capsule 10 is  
25 placed in a press device 101 of the HPHT system 100. The press device includes a die 102 that surrounds the periphery of the pressure cell, and opposed punches 103 that surround the end units, 11 and 12, of the pressure cell. Each of the die 102 and the opposed punches 103 apply pressure to the pressure cell during the gallium nitride growth process, in amounts sufficient to form gallium nitride crystals, as embodied by

the invention.

The end unit 12 comprises solvent and mineralizer 17 that are filled therein. The capsule 10 further includes a baffle structure 18 that is disposed between the end units, 11 and 12. The baffle structure 18 acts as a partial barrier and impedes free convection between the end units, 11 and 12. The baffle structure 18 includes at least one and possibly a plurality of apertures 19, and can be formed of a mesh, as long as it impedes free convection between the end units. Convection in each of the end units, 11 and 12, is free and stirs the reaction under the HPHT conditions, so as to result in an enhanced gallium nitride crystal growth rate, gallium nitride crystal uniformity, and gallium nitride crystal homogeneity.

Further, the end unit 11 is illustrated as containing a gallium nitride crystal 50. The crystal 50 is representative of a gallium nitride seed upon which further gallium nitride growth is achieved, or can be representative of a formed gallium nitride crystal that is being formed under the HPHT conditions, as embodied by the invention. Arrows 25 illustrate flow patterns that are believed to be formed in the end units, 11 and 12, of the pressure cell 10 under HPHT conditions.

The capsule 10 is generally formed of copper or a copper capsule with an inert-metal liner, since copper does not readily corrode or become embrittled by the HPHT reaction conditions, and also exhibits desirable cold-welding properties. Further, copper is a desirable material for the capsule 10 because it exhibits low permeability for hydrogen, which would have a deleterious effect on the HPHT apparatus if it leaked from the capsule. Alternatively, the capsule 10 may also be formed of platinum, since platinum will exhibit similar benefits as those discussed above with respect to copper.

The gallium nitride growth process, as embodied by the invention, will now be further described with reference to examples. These examples are not intended to limit the invention in any way. The dimensions, amounts, volumes, weights, and measured variables are provided in approximate units.

### EXAMPLE I

A copper capsule having with an internal volume of about  $0.04\text{cm}^3$ , is filled with approximately 0.017 grams (g) of poorly-crystallized source gallium nitride powder, about 0.012 g of  $\text{Li}_3\text{N}$  (mineralizer), and about 0.022 g of condensed ammonia (solvent). The capsule is then sealed, for example by cold welding. The sealed capsule is then placed within a pressure cell of a piston press assembly in a HPHT system. The pressure cell includes at least one of sodium chloride ( $\text{NaCl}$ ) and magnesium oxide ( $\text{MgO}$ ) pressure medium. A graphite indirect-heating tube is included in the pressure cell of the HPHT system. The pressure cell is then treated at an elevated temperature of about  $800^\circ\text{C}$  and an elevated pressure of about 25 kbar for about 1 hour.

At the completion of the elevated temperature and elevated pressure conditions, the pressure cell is cooled, and the pressure within the pressure cell is lowered. The contents of the pressure cell are recovered and washed, as discussed above. The final gallium nitride product comprises a fine white gallium nitride powder. Scanning electron micrographs of the gallium nitride powder before and after the gallium nitride growth process, as embodied by the invention, are provided in Figs. 4 and 5. Figure 4 illustrates untreated gallium nitride powder. Figure 5 illustrates gallium nitride having hexagonal features, which are characteristic of a hexagonal (wurtzite) crystalline lattice structure, in which the gallium nitride has been grown under a gallium nitride growth process, as embodied by the invention.

### EXAMPLE II

A second exemplary of the gallium nitride growth process, as embodied by the invention, uses a pressure cell and provides a temperature gradient to the pressure cell and its contents to grow gallium nitride crystals. In this process, a platinum capsule having an internal volume of about  $0.06\text{cm}^3$  is loaded with a reactant pill in a unit of the capsule. The reactant pill comprises approximately 0.017 g of poorly-crystallized gallium nitride powder, about 0.012 g of  $\text{Li}_3\text{N}$ , and about 0.001 g of  $\text{NH}_4\text{Cl}$ .

A partial barrier, or baffle, is disposed inside the capsule to be positioned on the pill. The baffle impedes free convection between the hot and cold ends of the capsule, when the pressure cell is heated, as embodied by the invention. Approximately 0.032 g of ammonia is condensed into the capsule. The capsule is  
5 then sealed a small distance above the baffle.

The capsule is disposed within a pressure cell, which includes NaCl and MgO pressure medium and a graphite indirect-heating tube. The pressure cell is disposed in a piston press assembly in a HPHT system. A temperature gradient is established in the pressure cell by positioning the capsule near the upper end of the  
10 pressure cell. This capsule position causes the upper end of the capsule to remain cooler than the lower end. The ends of the pressure cell are held at room temperature while a center portion of the pressure cell is heated by the graphite indirect-heating tube to a HPHT temperature.

Operation of the gallium nitride growth process under HPHT  
15 conditions with different hot zone temperatures provides different gallium nitride growth rates and growth results. For example, operation of a pressure cell containing poorly-crystallized gallium nitride powder,  $\text{Li}_3\text{N}$ ,  $\text{NH}_4\text{Cl}$ , and ammonia under HPHT conditions with a temperature of about  $800^\circ\text{C}$  for about 1 hour yields large white gallium nitride polycrystalline masses both above and below the baffle. An operation  
20 of a similar pressure cell under HPHT conditions at about  $600^\circ\text{C}$  for about 1 hour, results in the top end unit of the pressure cell containing large white gallium nitride polycrystalline masses, and gallium nitride powder that resembles the starting gallium nitride, as discussed above, in the other end unit.

While various embodiments are described herein, it will be appreciated  
25 from the specification that various combinations of elements, variations or improvements therein may be made by those skilled in the art, and are within the scope of the invention.



## CLAIMS:

1. A gallium nitride growth process for forming crystalline gallium nitride, the process comprising:

providing a source gallium nitride (15);

5 providing mineralizer (17);

providing solvent (17);

providing a capsule (10);

disposing the source gallium nitride, mineralizer and solvent in the capsule;

10 sealing the capsule;

disposing the capsule in a pressure cell (1); and

subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride onto at least one gallium nitride crystal.

15 2. The process according to claim 1, wherein the step of subjecting the pressure cell to high pressure and high temperature (HPHT) conditions comprises disposing the pressure cell in a high pressure and high temperature (HPHT) system (100).

3. The process according to claim 2, the method further comprising the steps of:

20 cooling the high pressure and high temperature (HPHT) system;

relieving the pressure in the high pressure and high temperature (HPHT);

and

removing the gallium nitride crystals from the high pressure and high temperature (HPHT) system.

4. The process according to claim 3, wherein the step of removing the gallium nitride crystals from the high pressure and high temperature (HPHT) system comprises:

washing the gallium nitride crystals in at least one of water and mineral acids.

5. The process according to claim 4, wherein the mineral acids are selected from hydrochloric acid (HCl) or nitric acid (HNO<sub>3</sub>).

6. The process according to claim 1, further comprising the step of:

forming a mixture comprising the source gallium nitride and at least one of the mineralizer and solvent, and then disposing the mixture in the capsule.

7. The process according to claim 6, further comprising the step of compacting the mixture.

8. The process according to claim 1, wherein the at least one gallium nitride crystal comprises at least one of gallium nitride crystal or gallium nitride boule.

9. The process according to claim 8, wherein the diameter of the gallium nitride crystal or gallium nitride boule is in a range from about 1 inch to about 6 inches.

10. The process according to claim 8, wherein the thickness of the at least one of gallium nitride crystals or gallium nitride boules is in a range from about 0.02 inches to about 12 inches.

11. The process according to claim 1, wherein the solvent comprises one of a nitrogen-containing solvent or an organic solvent.

12. The process according to claim 11, wherein the nitrogen-containing solvent comprises at least one of ammonia ( $\text{NH}_3$ ) or hydrazine, and the organic solvent is selected from methylamine, melamine, or ethylenediamine.

5 13. The process according to claim 1, wherein the step of subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride into at least one gallium nitride crystal comprises:

subjecting the pressure cell to pressures greater than about 5 kbar.

10 14. The process according to claim 13, wherein the step of subjecting the pressure cell to pressures greater than about 5 kbar comprises subjecting the pressure cell to pressures in a range from about 5 kbar to about 80 kbar.

15 15. The process according to claim 1, wherein the step of subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride into at least one gallium nitride crystal comprises:

subjecting the pressure cell to a temperature in a range between about 550°C to about 3000°C.

20 16. The process according to claim 1, wherein the mineralizer comprises at least one of alkali and alkaline-earth nitrides; amides; urea; ammonium salts; at least one of halide salts, sulfide salts, lithium salts, and nitrate salts; and combinations thereof, wherein the alkali and alkaline-earth nitrides are selected from  $\text{Li}_3\text{N}$ ,  $\text{Mg}_3\text{N}_2$ , or  $\text{Ca}_3\text{N}_2$ ; the amides are selected from  $\text{LiNH}_2$ ,  $\text{NaNH}_2$ , or  $\text{KNH}_2$ ; the ammonium salts are selected from  $\text{NH}_4\text{F}$  and  $\text{NH}_4\text{Cl}$ ; and at least one of halide salts, sulfide salts, lithium salts, and nitrate salts are selected from  $\text{NaCl}$ ,  $\text{Li}_2\text{S}$ , and  $\text{KNO}_3$ .

25 17. The process according to claim 1, wherein the mineralizers comprise

additives dissolved in solvents.

18. The process according to claim 1, wherein the step of providing a source gallium nitride comprises providing a crystalline gallium nitride.

5 19. The process according to claim 18, wherein the step of providing a source gallium nitride comprises providing a gallium nitride crystal seed (50) comprising a protective film that prevent dissolution of the gallium nitride prior to the step of subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride into gallium nitride crystals.

10 20. The process according to claim 1, wherein the step of subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride into at least one gallium nitride crystal further comprises creating a temperature differential within the pressure cell.

15 21. The process according to claim 20, wherein the step of creating a temperature differential within the pressure cell disposing a heat source (16) and the pressure cell proximate one another.

20 22. The process according to claim 20, wherein the step of creating a temperature differential within the pressure cell comprises at least one of asymmetrically disposing the source gallium nitride in the pressure cell at a higher temperature end of the pressure cell; providing an auxiliary heater to heat one end of the pressure cell; and providing a heating source (16) that generates differential heat to the source gallium nitride in the pressure cell.

25 23. The process according to claim 20, wherein the step of creating a temperature differential within the pressure cell comprises providing a heater (16) for the pressure cell proximate the source gallium nitride in the pressure cell with a thinner

heater element, whereby the thinner heater element generates more heat inside the pressure cell and heats up the source gallium nitride to create the temperature differential.

24. The process according to claim 1, wherein the step of providing a capsule comprises:

5                    providing a capsule that comprises two mating end units (11, 12), one of the end units being adapted to be disposed close to a heat source (16), and a baffle structure (18) that prevents free convection of heat between the end units during  
10                    subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride into at least one gallium nitride crystal.

25. The process according to claim 1, wherein the step of subjecting the pressure cell to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium  
15                    nitride into at least one gallium nitride crystal comprises disposing the pressure cell in a press device (100) that applies the high pressure conditions.

26. The process according to claim 25, wherein the step of disposing the pressure cell in a press device comprises disposing the pressure cell in a press device that comprises at least one of a die (102) and punch (103) that apply the high pressure.

27. The process according to claim 1, further comprising the steps of:

20                    compacting at least one of the source gallium nitride, a mixture comprising gallium nitride and solvent, gallium nitride and mineralizer, or a mixture comprising gallium nitride and solvent and mineralizer;

cooling the high pressure and high temperature (HPHT) system;

relieving the pressure in the high pressure and high temperature (HPHT);

removing the gallium nitride crystals from the high pressure and high temperature (HPHT) system; and

washing the gallium nitride crystals in at least one of water and mineral acids.

5

28. A gallium nitride crystal formed by the process according to claim 1.

29. A gallium nitride crystal formed by the process according to claim 27.

30. The process of claim 1, wherein the capsule comprises one of a copper capsule or a copper capsule with an inert-metal liner, and the step of disposing the source gallium nitride, mineralizer and solvent in the capsule comprises;

10

connecting the capsule (10) to a negative pressure manifold;

evacuating the capsule;

chilling the capsule to a temperature below room temperature;

admitting vapor-phase solvent to the manifold;

condensing the vapor-phase solvent in the capsule.

15

31. The process according to claim 30, wherein the step of sealing the capsule comprises:

closing off the capsule by at least one of pinching-off a section of the capsule to seal the capsule and closing a valve to the negative pressure manifold.

20

32. A gallium nitride growth process for forming crystalline gallium nitride, the process comprising:

providing a source gallium nitride (15);

- providing mineralizer (17);
- providing solvent (17);
- providing a capsule (10);
- combining the source gallium nitride with at least one of a mineralizer and  
5 a solvent to form a mixture;
- compacting the mixture;
- disposing the mixture the capsule;
- disposing at least one of mineralizer and solvent (17) to the capsule so the  
capsule comprises source gallium nitride, mineralizer, and solvent;
- 10 sealing the capsule;
- disposing the capsule in a pressure cell (1); and
- subjecting the pressure cell to high pressure and high temperature (HPHT)  
conditions for a length of time sufficient to dissolve the source gallium nitride and re-  
precipitate the source gallium nitride into at least one gallium nitride crystal;
- 15 cooling the high pressure and high temperature (HPHT) system (100);
- relieving the pressure in the high pressure and high temperature (HPHT);
- removing the gallium nitride crystals from the high pressure and high  
temperature (HPHT) system; and
- washing the gallium nitride crystals in at least one of water and mineral  
20 acids.

33. A gallium nitride growth process for forming crystalline gallium

nitride, the process comprising:

providing a capsule (10) that comprises two opposed end units (11, 12);

disposing source gallium nitride crystal seed in one end unit of the capsule;

5 disposing source gallium nitride with at least one of mineralizer and solvent in the other end unit of the capsule;

disposing solvent in each of the capsule end units;

10 subjecting the capsule to high pressure and high temperature (HPHT) conditions with a created temperature differential in a high pressure and high temperature (HPHT) system for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride onto at least one gallium nitride crystal.

34. The process according to claim 33, the process further comprising the steps of cooling the high pressure and high temperature (HPHT) system;

relieving the pressure in the high pressure and high temperature (HPHT);

15 removing the gallium nitride crystals from the high pressure and high temperature (HPHT) system; and

washing the gallium nitride crystals in at least one of water and mineral acids.

35. A gallium nitride crystal formed by the process according to claim 33.

20 36. A gallium nitride growth process for forming crystalline gallium nitride, the process comprising:

providing source gallium (15), wherein the source gallium comprises at



least one of liquid or solid gallium;

providing a capsule (10) that comprises two opposed end units (11, 12);

disposing the source gallium in one end unit of the capsule;

5 disposing the source gallium with at least one of a mineralizer and a solvent (17) to form a mixture, wherein mineralizer and solvent are disposed with the source gallium nitride by one of:

disposing the mineralizer and solvent individually to the source gallium nitride; or

10 disposing the solvent and mineralizer separately to the source gallium nitride;

subjecting the capsule to high pressure and high temperature (HPHT) conditions for a length of time sufficient to react the liquefied gallium with the ammonia under the HPHT growth conditions to form gallium nitride; and

15 subjecting the capsule to high pressure and high temperature (HPHT) conditions for a length of time sufficient to dissolve the formed gallium nitride and re-precipitate the source gallium nitride into at least one gallium nitride crystal.

37. The process according to claim 36, further comprising the steps of cooling the high pressure and high temperature (HPHT) system;

relieving the pressure in the high pressure and high temperature (HPHT);

20 removing the gallium nitride crystals from the high pressure and high temperature (HPHT) system; and

washing the gallium nitride crystals in at least one of water and mineral acids.

38. A gallium nitride crystal formed by the process according to claim 36.

39. A gallium nitride growth process for forming crystalline gallium nitride, the process comprising:

providing a source gallium nitride (15);

5 providing mineralizer (17);

providing solvent (17);

providing a capsule (10);

combining the source gallium nitride with at least one of a mineralizer and a solvent to form a mixture;

10 disposing the mixture to the capsule;

disposing at least one of mineralizer and solvent to the capsule so the capsule comprises source gallium nitride, mineralizer, and solvent;

sealing the capsule;

disposing the capsule in a pressure cell (17); and

15 subjecting the pressure cell to high pressure and high temperature (HPHT) conditions in a the high pressure and high temperature (HPHT) system for a length of time sufficient to dissolve the source gallium nitride and re-precipitate the source gallium nitride into at least one gallium nitride crystal;

cooling the high pressure and high temperature (HPHT) system (100);

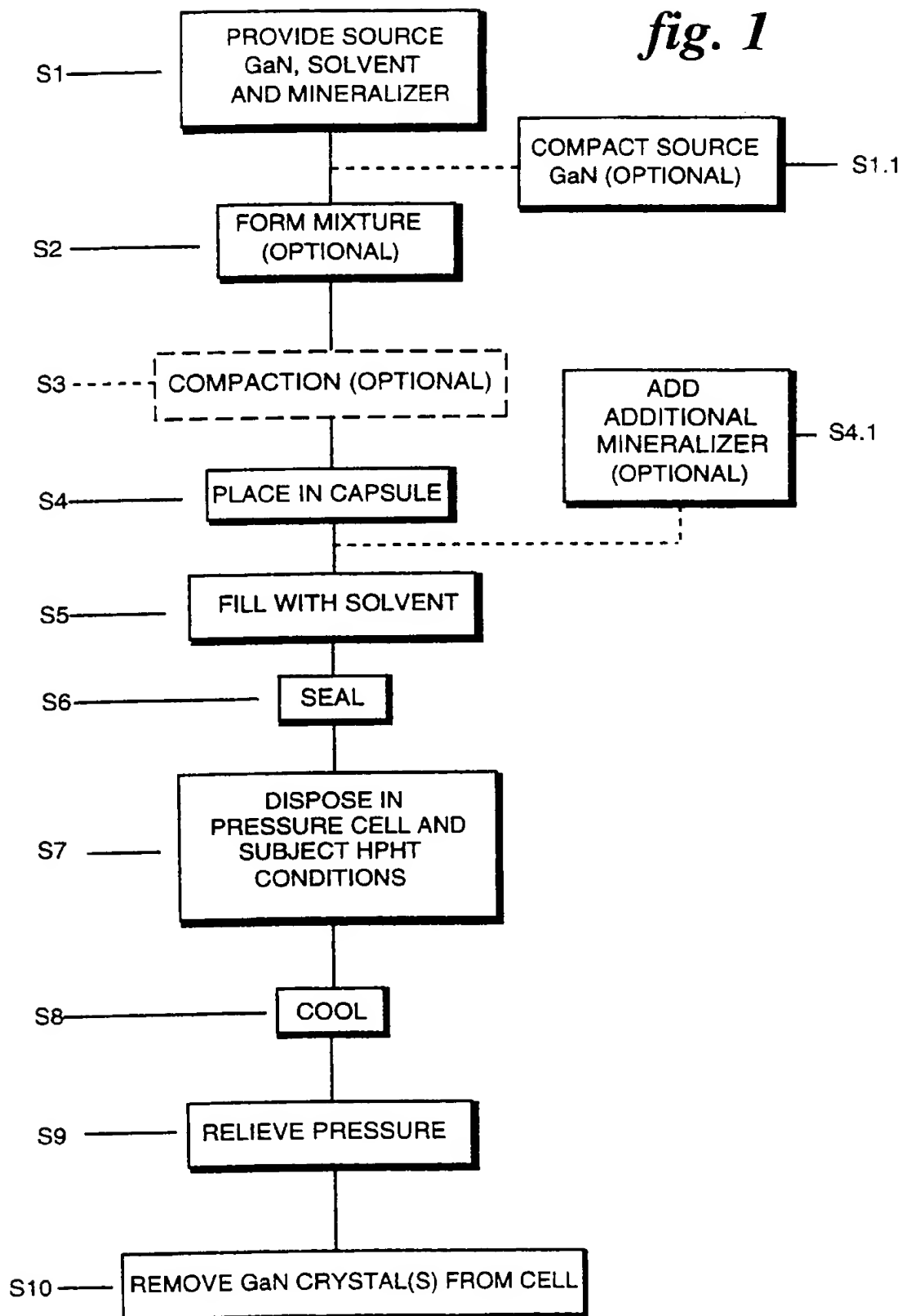
20 relieving the pressure in the high pressure and high temperature (HPHT);

removing the gallium nitride crystals from the high pressure and high

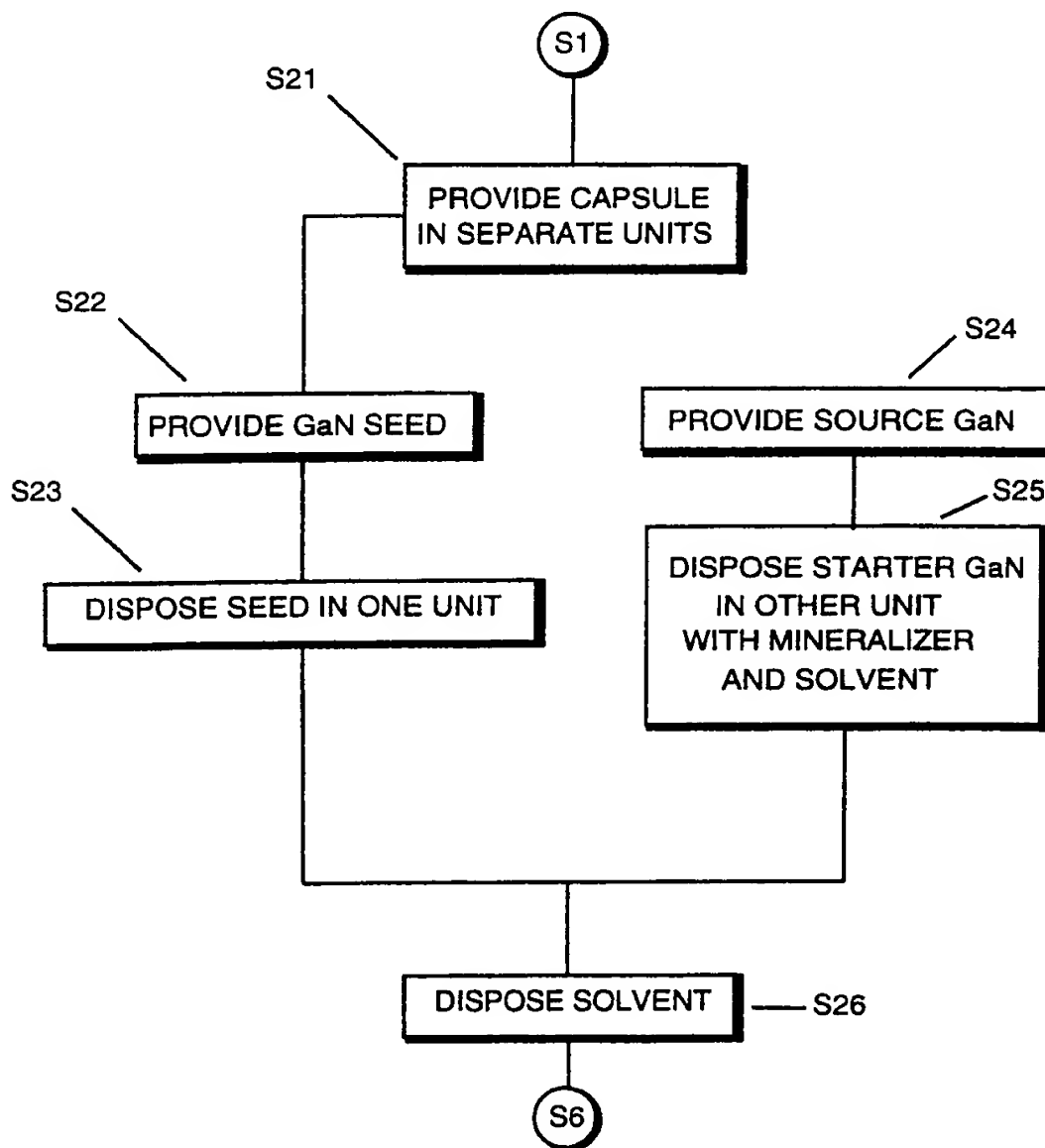
temperature (HPHT) system; and

washing the gallium nitride crystals in at least one of water and mineral acids.

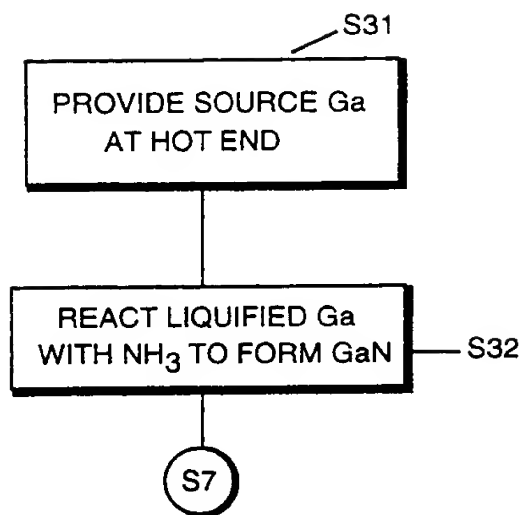
1 / 6

*fig. 1*

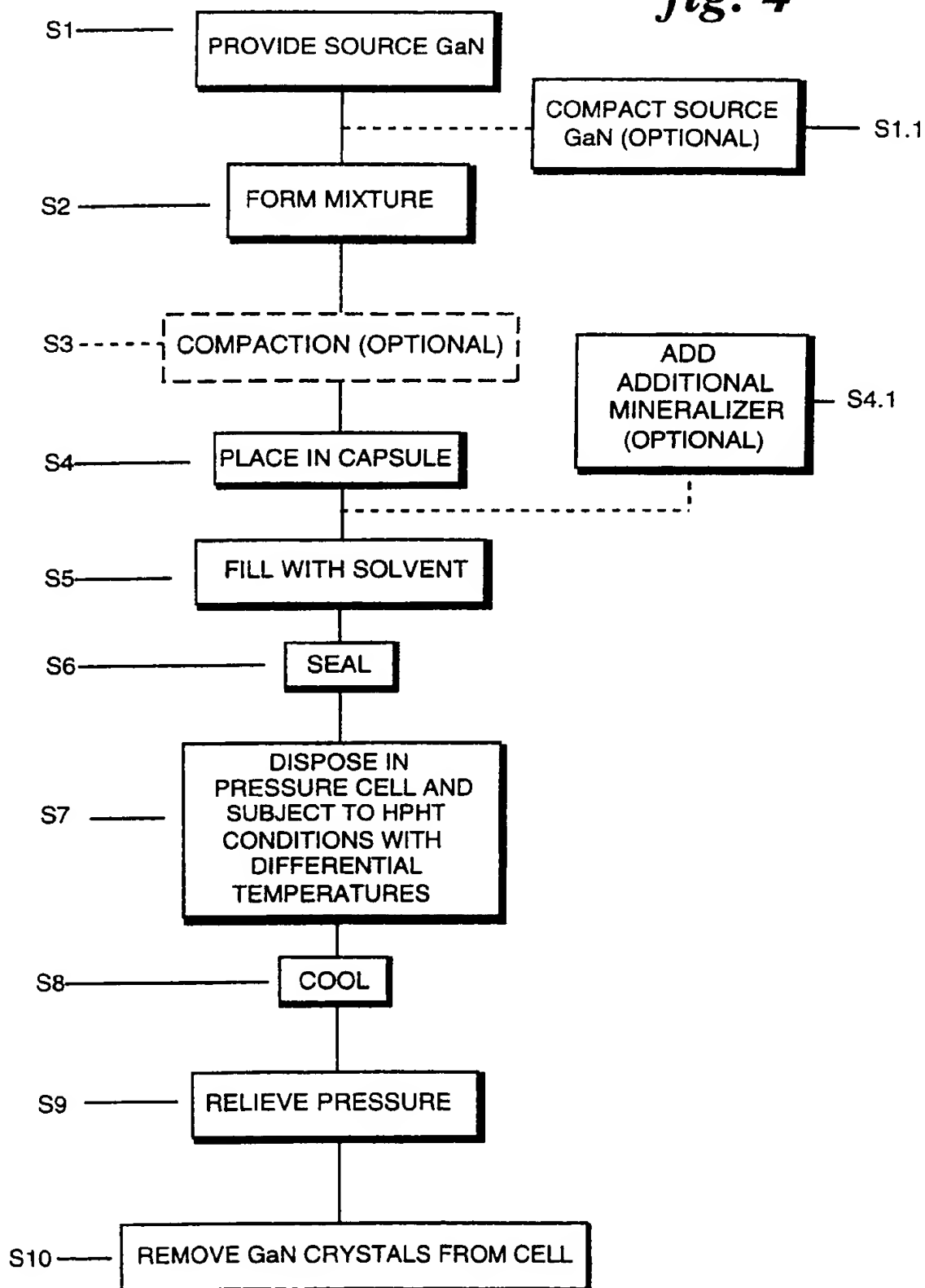
2 / 6

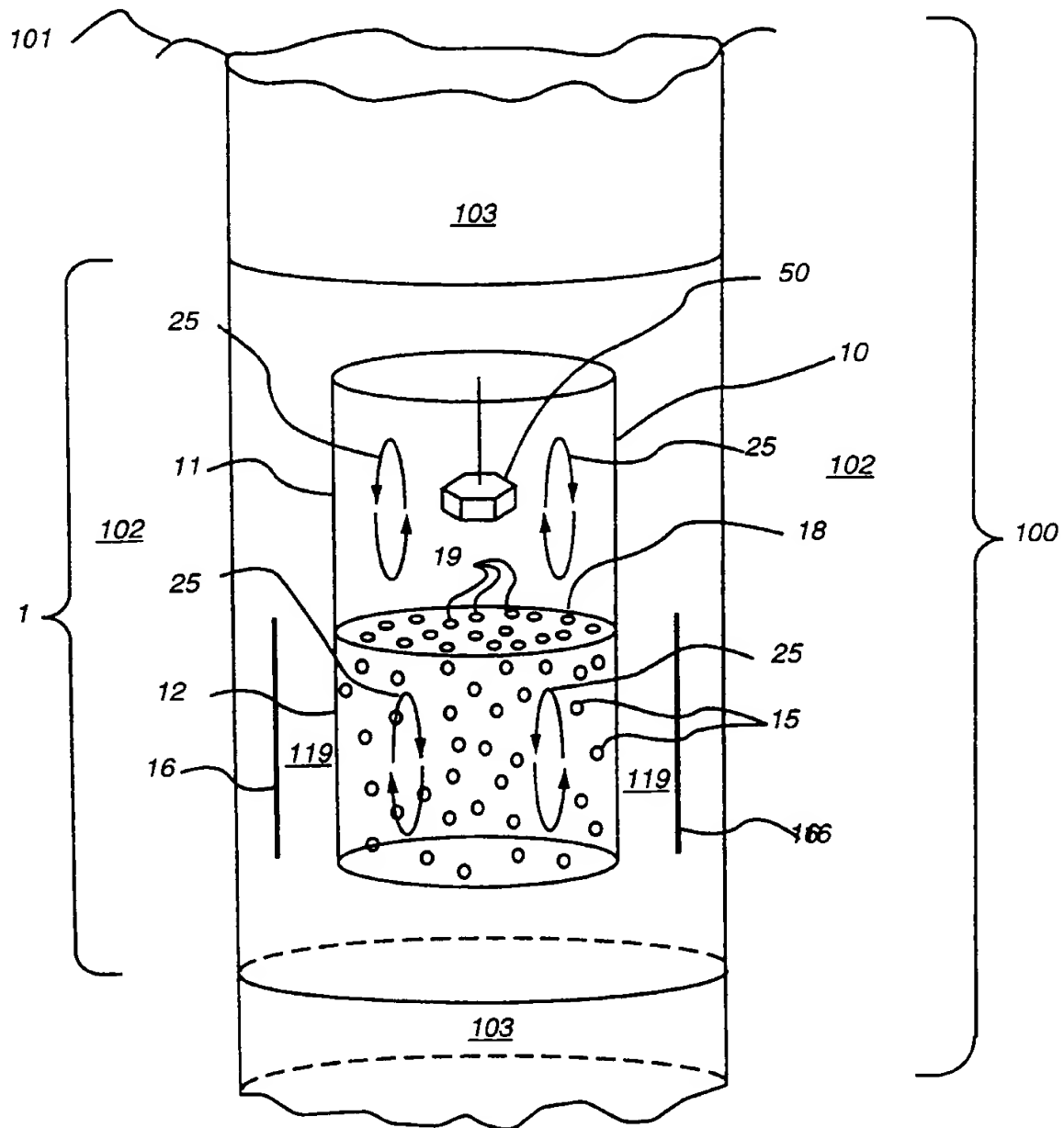
*fig. 2*

3 / 6

*fig. 3*

4 / 6

*fig. 4*



*fig. 5*



6 / 6

FIG. 6

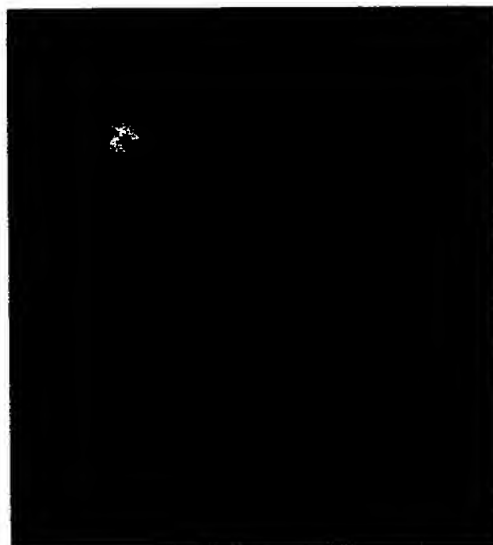
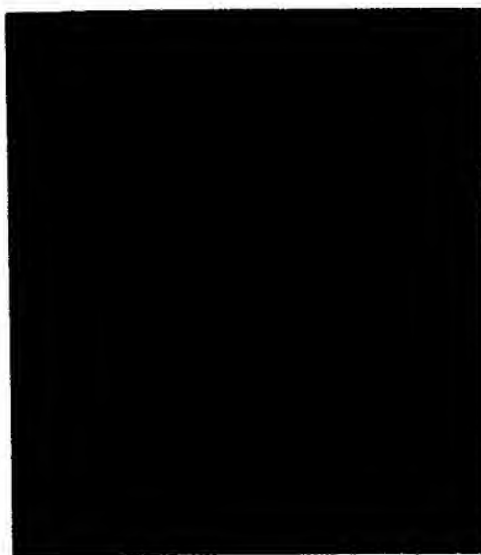


FIG. 7



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/26704

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 B01J3/06 C01G15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 B01J C01G C01B C30B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LESZCZYNSKI M ET AL: "The microstructure of gallium nitride monocrystals grown at high pressure" JOURNAL OF CRYSTAL GROWTH, NL, NORTH-HOLLAND PUBLISHING CO. AMSTERDAM, vol. 169, no. 2, 1 November 1996 (1996-11-01), pages 235-242, XP004049324 ISSN: 0022-0248	1-27, 32-34, 36, 37, 39
X	page 236 -page 237	28, 29, 35, 38
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 11, 30 September 1999 (1999-09-30) & JP 11 171699 A (FURUKAWA ELECTRIC CO LTD:THE), 29 June 1999 (1999-06-29) abstract	1-39

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- \*A\* document member of the same patent family

Date of the actual completion of the international search

16 January 2001

Date of mailing of the international search report

24/01/2001

Name and mailing address of the ISA  
European Patent Office, P.B. 5618 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Willsher, C

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/26704

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 937 790 A (NISHINO SHIGEHIO ;SUMITOMO ELECTRIC INDUSTRIES (JP)) 25 August 1999 (1999-08-25) the whole document ----	1-39
A	WO 96 41906 A (ADVANCED TECH MATERIALS) 27 December 1996 (1996-12-27) page 14, line 12 -page 15, line 10 -----	1-39

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int'l Application No

PCT/US 00/26704

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 11171699 A	29-06-1999	NONE	
EP 0937790 A	25-08-1999	JP 11209199 A US 6136093 A	03-08-1999 24-10-2000
WO 9641906 A	27-12-1996	NONE	